Copper Source Discrimination Using $^{65}Cu/^{63}Cu$ Isotope Ratios in San Francisco Bay Sediments

C.E. Dunlap[1], R. Williams[2], and A.R. Flegal[1]

1. Environmental Toxicology, WIGS, University of California at Santa Cruz, Santa Cruz, CA USA 95064

2. Lawrence Livermore National Laboratory, Livermore, CA, USA

Recent reports have indicated that differences in copper isotopic compositions can be analytically distinguished in environmental matrices [1-4]. Since copper is widely used in human industry [5, 6] and is toxic to phytoplankton at low ambient concentrations [7-9], the potential use of its isotopic variation as a tracer is of considerable interest.

In San Francisco Bay, copper contamination in sediments and in the water column is pandemic. This problem is leading to large-scale regulatory efforts on the part of the US Environmental Protection Agency, California State Water Resources Control Board, and local municipalities to limit inputs of copper to the Bay. Their efforts are being confounded by fundamental gaps in knowledge of the sources of the copper and of its biogeochemical cycling within the Bay. However, those questions could be addressed with studies of stable copper isotopic compositions, as we have done with lead, using the isotopic compositions to fingerprint industrial and natural sources and clarify biogeochemical cycling within the Bay [10, 11].

In order to validate that approach, four samples were taken from surface sediments collected on a north-south transect in the Bay, and eight samples were taken from a gravity core (SPB-1) collected in a region of the Bay (eastern San Pablo Bay) that has been well studied for depositional chronology and variation in lead concentration and isotopic composition [12-15]. The lead variations chronicle natural and anthropogenic inputs and biogeochemical cycles within the estuary over the past 150 years [15], providing a point of comparison for assessing the significance of any measured variation in copper isotopes.

Stable copper isotopic compositions ($^{65}Cu/^{63}Cu$) in San Francisco Bay surface sediments are heterogeneous, suggesting that the copper is not derived from a single source. Comparison of those surface sediment ratios with ratios in the SPB-1 sediment core from northern San Francisco Bay reveals three primary sources of copper inputs to the estuarine system: natural background sediment (represented by the core bottom), historic hydraulic mining sediment (beginning at approximately 120 cm depth in the core), and modern industrial sources (seen in the surface sediments). Since copper concentrations in the Bay remain relatively high despite orders of magnitude reductions in point source discharges of copper, the current heterogeneity of copper isotopic compositions in surface sediments suggests that there have been multiple, relatively large inputs of industrial copper to the system over the past four decades. Based on simple mass balance calculations, these include copper in anti-fouling marine paints, biocides, plumbing, and brake pad detritus. While the isotopic compositions of those sources have not been characterized, the presence of measurable differences in copper isotopic compositions within the Bay indicates that the sources of that copper may be resolved with additional isotopic composition analyses.

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